Study of Polypropylene/Polybutene blends modified by gamma irradiation and (High Melt Strength Polypropylene)/Polybutene blends.

Adriana Yoshiga[a], Harumi Otaguro[a], Luís Filipe C.P. Lima[a], Beatriz W. H. Artel[b], Duclerc F. Parra[a], Jeferson Rodrigues Bueno[a], Rodrigo Shinzato[a], Marcelo Farrah[c], Ademar B. Lugão[a].

[a]Instituto de Pesquisas Energéticas e Nucleares IPEN/CNEN, Av. Lineu Prestes 2242, Cidade Universitária, CEP 05508-900, São Paulo-SP, Brazil
[b]Empresa Brasileira de Radiação, Av. Cruzada Bandeirante, 269, CEP 06700-000, Cotia-SP, Brazil
[c]BRASKEM, III Pólo Petroquímico, Via Oeste, Lote 5, CEP 95853-000

Abstract

It is well-known that polypropylene (PP) is difficult to process as a consequence of its linear structure. It is also known that grafting of long-chain branches on PP backbone using ionizing radiation is an effective approach to achieve high melt strength polypropylene (HMS PP). Chain-scission and, in minor extend, crosslinking and grafting are the predominant reaction in order to branch PP backbone. However, if multifunctional monomers are used to promote the grafting reaction, crosslinking can surpass chain scission and grafting, reducing drawability. Therefore, in an effort to enhance the processability and so the drawability, it has been found helpful to add a small amount of polybutene-1. Gamma irradiation technique was used to induce chemical changes in blends of PP and polybutene in acetylene atmosphere (crosslinker promoter) and in HMSPP/polybutene blends. The samples were irradiated with a ^{60}Co source with doses of 12.5 and 20 kGy in the presence of acetylene. In this work, two different methods of blends processing were compared regarding rheological and mechanical properties. Effects on the strength and elongation at the yield point and at rupture were observed by mechanical tests and showed decrease of tensile strength and increase of elongation at rupture for samples obtained by irradiation of blends. The results from rheology demonstrated an increase in melt strength and drawability of blends.

Key words: Polypropylene, high melt strength, polybutene-1, blends.

1. Introduction

Radiation processing is very useful to improve properties of polymer materials by balancing grafting, crosslinking and chain scission reactions. Polypropylene (PP) has been applied to a wide range of production due to its various excellent properties such as high stiffness, chemical resistance, no environmental pollution when incinerated, low specific density and good mechanical properties at low price. Therefore PP has been preferred to polyvinylchloride, polyurethane and polyethylene in a wide range of applications. However, PP has low melt strength as a consequence of its linear structure. The lack of strain hardening makes the processability of this material into foams, films and fibers at high production rate very complicated and sometimes impossible [1-4].
High melt strength polypropylene (HMS PP) has been recently developed and introduced in the market by the major international polypropylene producers. Various methods have been applied to modify polypropylenes by the addition of long chain branches. BRASKEM, a Brazilian PP producer, together with EMBRARAD, Brazilian gamma-irradiator, and the Nuclear and Energy Research Institute (IPEN) polymer group jointed forces to develop a national technology for the production of HMS PP. This technology is based on the grafting of long chain branches on PP backbone using acetylene as crosslinker promoter under gamma radiation, generated from a Co^{60} source. The radio-induced grafting reactions occur on account of the rearrangement of radicals formed in polymer materials, however, if multifunctional monomers are used, the kinetics of crosslinking can be increased and eventually the melted polymer under processing will be too elastic with poor drawability [5].

Schemm et al [6] informed that polybutene melt strength is ca. twice as high as for PP with closer melt flow index, witch results in better drawability and less sagging of the melt during extrusion. Nowadays, an important approach to the development of polymer materials is based on the combination of different two or more polymers into a new product having some of the desired properties of each component. One of the main obstacles to achieve this target is the inherent incompatibility of most polymer combinations, resulting in the deterioration of mechanical properties of the blends.

The polybutene like polyethylene and polypropylene is a polyolefin, consequently has typical properties of commodities polymers, and however has properties of engineering polymers too. It can be used as a component blend component to improve and differentiate the properties of other polyolefins. In PE films, polybutene can improve sealing performance, the ability to peel with controlled force, flexibility and temperature strength. Due to its similar structure, polybutene is compatible with PP and it can be used in blends to improve certain characteristics of PP. Polybutene is used to modify PP fibres to enhance softness, and flexibility. There are relatively few studies on polybutene blends, among which that of Shie et al [7], who studied the crystallization behavior and the morphology of polypropylene/polybutene blends. On the other hand, studies of irradiated polybutene blends have not been found yet [7-11]. It is known that the main effect of polybutene irradiation is the chain scission [12-13].

In this work, polybutene was blended with PP and then these blends were modified with gamma radiation in presence of acetylene to improve melt strength and drawability. Blends of polybutene and HMS-PP were studied too.

The use of radiation in mixtures of polypropylene with polybutene in order to improve the drawability and melt strength can have great industrial interest.

2. Experimental

Materials

The polypropylene used in this study (MFI: 1.5 g/10 min) was supplied in a granular form and was mixed with polybutene (MFI: 6.7 g/10 min). Blends with 10 and 20wt% of polybutene were prepared by two different methods (Table 1). These compositions were chosen due to the fact that polybutene presents high price.

In the method 1 (Figure 1a), the polypropylene was blended with polybutene and after that the blends were irradiated with gamma rays with doses of 12.5 and 20 kGy in presence of acetylene.

In the method 2 (Figure 1b), the acetylene was injected in bags of nylon with polypropylene inside. These samples were irradiated with doses of 12,5 and 20 kGy of gamma rays (^{60}Co source) at Embrarad and then modified polypropylene was blended with polybutene.

Insert Figure 1

Insert Table 1

Analysis

Melt index and swelling ratio

The melt flow indexes of the blends were measured in a Melt flow equipment of CEAST where the samples were flowed through an orifice of 2.00 mm diameter under a loading of 2.16 kg at 230°C (ASTM D 1238-04c). The swelling ratio was calculated by diameter ratio of this material to 2.00 mm.

Gel content

Gel content of the samples was determined by extracting the soluble components in boiling xylene for 12 hours at 135°C. Then the residue was dried to constant weight during 1 hour at 150°C. Three species were used to determine the average gel content for each sample (ASTM D 2765-01).

Mechanical properties

A EMIC DL 300 universal tensile/compression testing machine equipped with a data acquisition system was utilized to carry out the tensile tests. The speed velocity of testing was 50 mm/min and the tests carried out at a temperature of 23°C. At least six specimens were tested from each sample, complying with ASTM D 638-03 standard.

Rheological characterization in shear flow

The rheological measurements in shear were performed at a temperature of 200°C using rotational Physica rheometer (MCR 300) with plate-plate geometry of 25mm in diameter and a gap of 1.0mm. Samples of a thickness of 1.2 and diameter of 25mm were prepared from the irradiated and stabilized pellets in a hot press at a temperature of 190°C.

Melt strength and drawability

In the rheotens test, the tensile force needed for elongation of an extruded filament was measured as a function of the draw ratio. The sample was extruded at 190°C in a Haake reometer (single screw diameter) in combination with a Rheotens Mod. 71.97 (Göttfert). The test velocity varied between 40.0 and 575.0 mm.s^{-1} and acceleration was 6 mm.s^{-2}. It can be assumed that cooling of the extruded strand in the spinline is small, so the polymer melt is elongated under isothermal conditions.

3. Results and discussion

Table 2 ilustrates the influence of radiation process and presence of acetylene monomer on phenomena like chain scission, grafting and crosslinking, expressed by melt flow index, gel fraction, melt strength and drawability. PP is difficult to crosslink by radiation, because the crosslinking and chain scission reactions proceed at almost same rate. It is known that the efficiency of crosslinking is improved by adding multi functional monomers like acetylene, which have carbon-carbon double bond in its molecule. From results, it was revealed that the addition of polybutene with PP increased significantly the drawability, however occurred a drastic decrease of melt strength. Higher values of melt strength and drawability were obtained for irradiated PP/polybutene blends with acetylene in relation of pure PP, the samples C and D showed better results. The slight increase of gel fraction of these samples may be attributed probably to the grafting with consequent branching and crosslinking, however an increase of melt flow index was observed probably due to polybutene addition.

The samples E, F, G and H prepared by blending of HMS PP and polybutene showed a slight decrease of melt flow index in relation of HMS PP with consequent increase of gel fraction for samples G and H that may be attributed to a possible chain entanglement between HMS PP and polybutene. This chain entanglement favored the flow in Rheotens with consequent increase of drawability, however showed higher shear strength with consequent increase of complex viscosity that will be observed in Figure 2. All samples prepared by method 2 showed a decrease of melt strength with slight increase of drawability in relation of HMS PP.

Insert Table 2

The tensile strength and elongation at maximum are shown in table 3. Samples A, B, C and D showed a decrease of tensile strength and an increase of elongation after irradiation. The same behavior was observed at rupture.

Samples E, F, G e H showed a decrease of maximum tensile strength in relation of pure PP, however these values were closer to results of HMS PP and the elongation showed a slight increase. All samples obtained by Method 2 showed remarkable decrease of tensile strength and elongation at rupture in relation of pure PP and HMS PP.

Insert Table 3

The complex viscosity plotted as a function of angular frequency is shown in Figure 2. At low shear rates PP melts show a Newtonian behavior with a constant viscosity (plateau). The viscosity in the Newtonian regime is called the zero shear viscosity, η_o that gives valuable information of molar mass. The plateau was observed only for pure resins and blends without irradiation. In fact, the slope of the flow curves of all blends studied became steeper, especially for samples A, D, E and F. It is well known that this is the typical behavior of a branched polymer that can be observed also in curves of HMS PP. All irradiated blends showed complex viscosity values lower than the values of pure PP in the angular frequency studied, denoting degradation process.

Insert Figure 2

4. Conclusions

To improve melt strength and drawability, PP was blended with polybutene and irradiated in presence of acetylene. PP irradiated in presence of acetylene (HMS PP) was as well as blended with polybutene. The tests reveal structural modifications on blends studied. It was observed that only the blended of polybutene with polypropylene without irradiation process improved the drawability, however the melt strength showed a significant decrease. The irradiation used in method 1 and method 2 increased the melt strength and drawability in relation of pure PP.

Even the increase of melt strength, the mechanical properties decreased for irradiated blends. This usually occurs in blends with heterogeneous structure due to the weak interfacial adhesion between components of the blend, the imposed stress cannot be sufficiently transferred between the different phases, however the blends no irradiated showed values of mechanical properties closer to results pure PP, so the decrease may be attributed to irradiation process.

5. References

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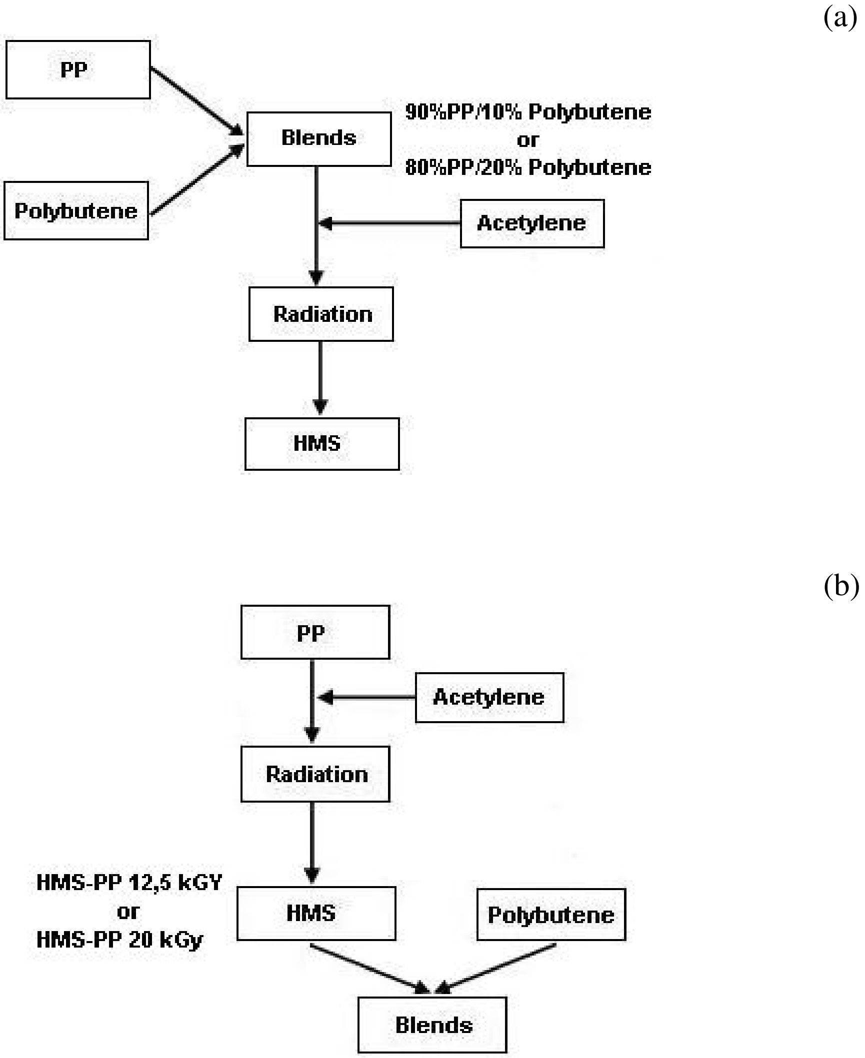

Figure 1- Methods of PP/Polybutene blends preparation : (a) method 1 and (b) method 2.

Table 1 - Formulation of blends.

Sample/Method	Polypropylene/Polybutene (wt%)	Dose (kGy)
A/1	90/10	12,5
B/1	80/20	12,5
C/1	90/10	20,0
D/1	80/20	20,0
Sample/Method	HMS-PP/Polybutene (wt%)	Dose (kGy)
E/2	90/10	12,5
F/2	80/20	12,5
G/2	90/10	20,0
H/2	80/20	20,0

Table 2 - Results of melt flow index, gel fraction, melt strength and drawability.

	Melt flow index (g/10 min)	Gel fraction (%)	Melt strength (cN)	Drawability (mm/s)
PP	1,5	0	20,4	7,4
Polybutene	6,7	0	5,5	9,4
90%PP/10%Polybutene	3,9	0	1,3	30,0
80%PP/20%Polybutene	4,9	0	1,4	35,0
A (90/10)	3,0	5,2	21,9	13,7
B (80/20)	3,9	4,7	29,9	8,8
C (90/10)	3,2	8,7	37,8	12,2
D (80/20)	2,6	6,4	41,2	11,6
HMS PP 12,5 kGy	2,5	1,9	58,6	10,8
HMS PP 20 kGy	2,9	1,7	53,0	12,0
E (90/10)	2,1	2,9	32,5	13,1
F (80/20)	2,1	1,7	32,6	14,5
G (90/10)	2,0	6,8	35,1	12,5
H (80/20)	2,1	6,4	33,5	12,4

Table 3 – Results of tensile at rupture, deformation at rupture, maximum tension and maximum deformation.

	Tensile at yield point (MPa)	Elongation at yield point (%)	Tensile at rupture (MPa)	Elongation at rupture (%)
PP	28,9 ± 0,7	10,6 ± 1,0	18,8 ± 1,4	640,6 ± 13,6
Polybutene	7,2 ± 1,1	11,0 ± 1,0	18,6 ± 1,1	367,6 ± 13,6
90%PP/10%Polybutene	23,8 ± 1,7	9,2 ± 1,3	28,8 ± 1,7	654,8 ± 25,8
80%PP/20%Polybutene	20,0± 0,3	11,1 ± 1,3	25,9 ± 0,2	582,4 ± 22,9
A (90/10)	22,1 ± 0,7	16,7 ± 0,9	15,6 ± 2,8	777,9 ± 93,9
B (80/20)	21,1 ± 0,5	15,1 ± 0,5	18,3 ± 0,8	716,5 ± 50,1
C (90/10)	21,2 ± 1,1	14,0 ± 1,7	13,3 ± 2,7	756,7 ± 77,2
D (80/20)	20,7 ± 0,6	14,2 ± 1,9	16,6 ± 2,2	768,0 ± 63,6
HMS PP 12,5 kGy	25,2 ± 0,7	6,2 ± 1,0	22,0 ± 1,4	639,4 ± 13,9
HMS PP 20 kGy	25,5 ± 0,6	6,1 ± 1,8	18,9 ± 2,0	622,4 ± 27,4
E (90/10)	24,9 ± 0,6	10,9 ± 1,6	13,7 ± 1,6	581,1 ± 87,3
F (80/20)	24,0 ± 1,8	7,1 ± 1,2	15,2 ± 1,1	513,8 ± 29,8
G (90/10)	22,6 ± 1,1	9,7 ± 1,3	12,0 ± 1,2	552,4 ± 25,8
H (80/20)	22,8 ± 1,3	8,6 ± 1,1	15,6 ± 2,7	486,2 ± 30,9

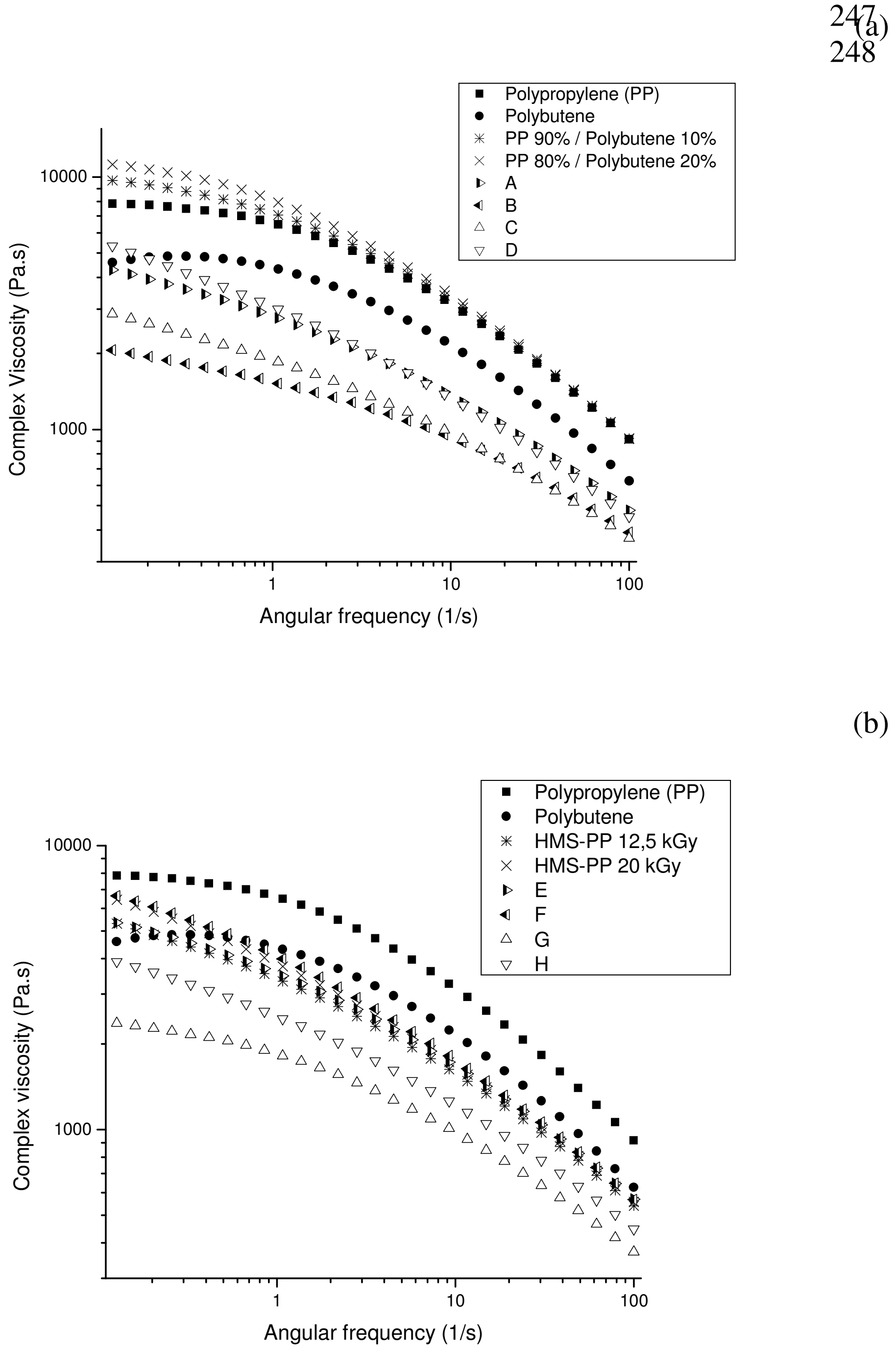

Figure 2 - Complex viscosity as a function of frequency angular for samples: (a) processed by method 1 and (b) processed by method 2.